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Effect of trace elements on carbonate thermodynamic constants

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Abstract

This study is a preliminary work on the description and the modeling of mechanisms potentially causing discrepancies between experimental data and thermodynamic calculation performed on carbonate equilibrium at high temperature. A better understanding of dolomite dissolution/precipitation processes that occur during its equilibration is important for investigations of high-level radioactive waste disposal or Carbon and Capture Storage (CCS). The first results demonstrated the fast dolomite equilibration in solution (within 12 days) and the good agreement between experimental and thermodynamic calculations at 25 °C for dolomite and calcite-dolomite systems whereas discrepancies are observed at higher temperature (80 °C). As shown from cathodoluminescence photomicrographs, one of the expected mechanisms causing those differences is the incorporation of trace elements such as Mg, Mn or Ba found in natural systems.

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Keywords: dolomite; calcite; water/rock interactions; traces elements; manganese; barium.

1. Introduction

The carbonate system is one of the most reactive mineralogical assemblages of clay-rocks. Consequently, pristine clay-rock pore water compositions are expected to be at equilibrium with carbonate minerals. However, it is difficult to fully reconcile the aqueous concentration data obtained from seepage water sampled from in situ boreholes with the equilibrium concentrations obtained from pore water modeling [1]. It is especially true for dolomite whose solubility spans a large range of values in thermodynamic databases as a function of crystallinity considerations, and

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for siderite/ankerite or other Fe-bearing carbonates whose compositions influence their solubility. The understanding of the carbonate system in clay-rock is necessary for a number of predictions including the effect of an increase of temperature on the pore-water chemistry.

Current pore-water equilibrium models [1, 2] consider that divalent cations such as Ca, Mg and Fe are controlled by equilibrium reaction with pure carbonates: calcite for Ca, dolomite for Mg and siderite for Fe. The Ca/Mg ratios measured in pore water compared to the ratios calculated from thermodynamic equilibrium with pure calcite/pure dolomite indicate that this is a reasonable assumption for Callovian-Oxfordian (COx) clay rock [3] but not for the Opalinus clay [4, 5]. Besides, petrological and chemical studies of carbonate minerals in these clay formations showed that several generations of calcite and chemical evolution of calcite and dolomite with diagenesis [3, 6], a complexity that is not accounted for in modeling studies.

In this respect, experiments were conducted to study the kinetics of equilibration in solution of dolomite and carbonate mineral assemblages at 25 and 80°C. Dolomite and calcite-dolomite systems were investigated and the results were then compared to thermodynamic calculations. The incorporation of trace metals in the mineral structures was followed through cathodoluminescence (CL) measurements.

2. Materials and methods

A natural dolomite and a synthetic calcite [7] were selected for this study. Natural blocks collected in the field were crushed to centimeter length; impurities visible optically were removed before crushing the sample to a lower size (< 12 microns). Microprobe and X-Ray Diffraction (XRD) analyses of pristine minerals were performed to check the phase's purity and avoid the presence of detectable secondary phases. XRD patterns revealed that only dolomite and calcite were present in the powders. ICP-AES and microprobe analyses evidenced the presence of 0.2 at% of Mg in the synthetic calcite whereas dolomite was Ca enriched (Ca/Mg = 1.06) and contained Fe (cf. Table 1) and also Ba impurities (ICP-AES: 1.4g kg⁻¹). The presence of such impurities was expected as the dolomite sample was natural.

Batch equilibration tests were performed with synthetic calcite in contact with dolomite in Nalgène® (polycarbonates or polysulfones) reactors at 25 °C and 80 °C. The solid over liquid ratio was 10 g L⁻¹. Solutions were prepared with pure water (resistivity: 18.2 MΩ cm) for dolomite experiments and from analytical grade salts: NaCl, MgCl₂·6H₂O, CaCl₂·2H₂O, NaHCO₃ for mixed experiments. One reactor was used for each sample time in order to performed solid characterization as well as solution analyses.

The pH measurement of batch solutions was carried out with a Mettler Toledo, seven multi pH meter using NIST 4, 7 and 9 buffers. Cations (Ca²⁺, Mg²⁺) were analyzed in solutions by ionic chromatography. The element concentrations in solution were determined with an uncertainty of 5%. Alkalinities were calculated with the Gran method described by Neal [8]. Then, the final powders were characterized by XRD to control potential secondary phases formation, but also by Transmission Electron Microscopy (TEM) and by CL.

Saturation indices calculation were performed with PHREEQC v3 [9] using the ThermoChimie [10] database.

Table 1. Microprobe analyses of major elements constituting pristine minerals used in this study (coefficients have to be divided by 5 to obtain atomic percent as they are calculated using the following theoretical formulae: CaCO₃ and Ca_{0.5}Mg_{0.5}CO₃).

Mineral	Ca	Fe	Mg
Synthetic calcite	0.990	0.000	0.009
Dolomite	0.512	0.003	0.485

3. Results and discussion

3.1. Dolomite dissolution

The solution composition in contact with dolomite reached an almost steady state within 12 days at 25 and 80 °C.

At 25 °C, the experimental data were consistent with the thermodynamic modeling performed with PhreeqC using the ThermoChimie database (Fig. 1.a) and the solution composition evolved only slightly after 30 days to reach the calculated values. At 80 °C, discrepancies were observed; Ca and Mg concentrations as well as alkalinity were underestimated by the calculation while pH was overestimated (cf. Fig. 1.b). Similar results were obtained using the Thermoddem database [11]. At both temperatures only a very little incongruence between Ca and Mg was observed: the Mg concentrations released in solution were 6 to 8 % lower than the Ca concentrations. Those values remained close to the analytical uncertainties (5 %).

Saturation indexes calculated at 25 °C showed that the solution was undersaturated with respect to calcite, dolomite and magnesite. At 80 °C, calcite and dolomite remained undersaturated while magnesite was oversaturated since the 12th day of reaction. Thus, magnesite could be an expected secondary phase. Unfortunately, this precipitation could not be identified with X-ray diffraction (XRD) or transmission electron microscopy (TEM), possibly because a small amount precipitated. However EDX analyses performed with TEM showed modifications of the Ca/Mg ratio that varied from 0.85 to 1.20 with an average value of 1. These results highlighted the complexity of the dolomite dissolution process that could be influenced among others parameters by the traces present in its structure. To show the potential effect of trace elements on the equilibria in the carbonate system, calcite-dolomite systems were investigated to monitor changes in composition of a pure synthetic calcite in the course of dolomite dissolution and calcite re-equilibration with the water composition.

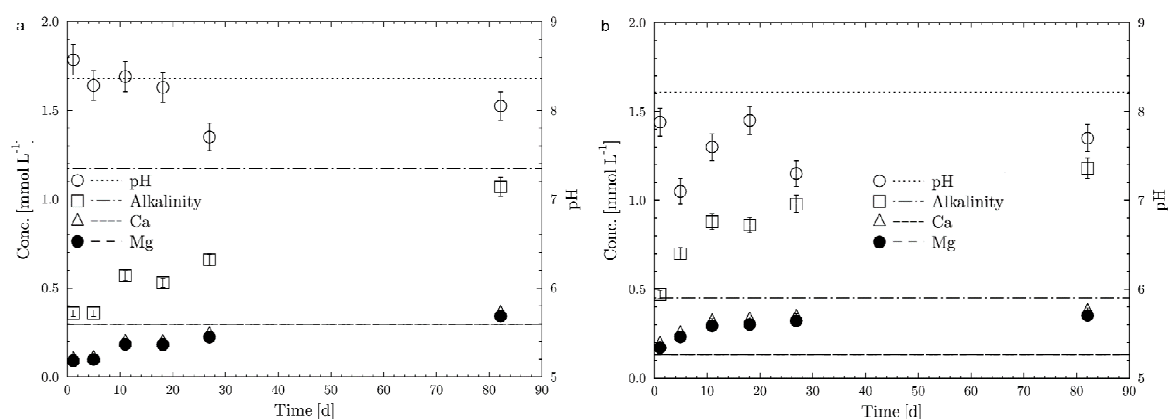


Fig. 1. Ca, Mg, alkalinity (in mmol L⁻¹) and pH in solutions during dolomite dissolution (a) at 25 °C, (b) at 80 °C and comparison with thermodynamic calculation performed with the ThermoChimie database [10] (symbols are experimental points and lines are modelling results for dolomite equilibrium in pure water; modelled Ca and Mg concentrations are equal).

3.2. Calcite-dolomite equilibrium

We examined the incorporation of trace elements in a synthetic calcite having only a slight amount of magnesium in its structure. Solutions analyses were consistent with thermodynamic calculations performed at 25 °C. XRD and TEM diffraction pattern did not show any modification of phases. However, EDX measurements showed that Mg content in calcite varied between 0.48 and 1.70 at%. This result is in agreement with a Mg enrichment in the calcite structure; nevertheless the presence of dolomite on the TEM grid could also explain this little Mg enrichment because of the size of the spot for EDX analysis.

The CL photomicrographs of the mixed powder (calcite-dolomite) showed that modifications occurred in the calcite structure. Before the experiment, pristine synthetic calcite displayed a dark blue color and the pristine dolomite appeared red (cf. Fig. 2a and b). At the end of the experiment, calcite and dolomite could not be discriminated in the mixed powder that displays an orange color indicating incorporation into the calcite particles (Fig. 2.c). As Fe is an inhibitor of the luminescence, its incorporation could not explain the calcite luminescence. Only Mg and others impurities such as Ba or Mn coming from the dolomite can explain such a luminescence. Among those elements Mn is the most luminescent activator. Even if Mn could not be detected by microprobe or

ICP measurements in pristine dolomite, it could have been present in very low amount, thus explaining the luminescent signal in calcite [12].

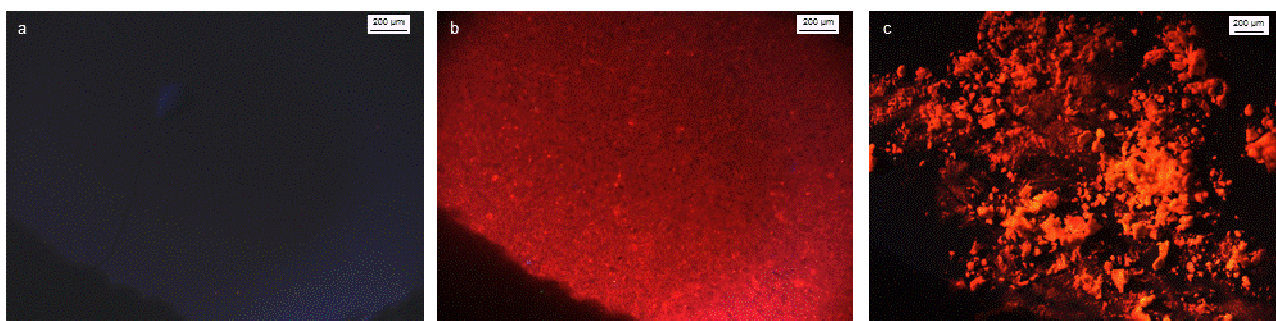


Fig. 2. CL photomicrographs of studied minerals; a: dark blue pristine synthetic calcite pellet (gain 6, laying time 1s, x40), b: red natural dolomite pellet (gain 6, laying time 1s, x40), c: final yellow-orange powder of mixed calcite-dolomite system (gain 6, laying time 1s, x50).

4. Conclusion

Dolomite-solution equilibrium was established in 12 days as expected from previous studies [13, 14]. Dolomite displayed an almost congruent dissolution that yielded solution compositions that were consistent with thermodynamic calculations at 25 °C. Higher discrepancies were observed at 80 °C where Ca, Mg and alkalinity were underestimated. These differences did not seem to originate from secondary phases precipitation but could be linked to trace metal incorporation, with a higher influence on the solubilities and dissolution/precipitation congruency at 80 °C than at 25 °C. This assumption was supported by calcite-dolomite experiments that showed structural modification observed through a modification of the calcite luminescence.

However, those processes need now to be quantified; a task that remains difficult in a mixed carbonates system.

Acknowledgements

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